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Effect of Intra- and Intermolecular Interactions on Solution Properties of Sulfonated Polystyrene Ionomers

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ABSTRACT: The role of intra- and intermolecular interactions on solution properties of sulfonated polystyrene ionomers was studied in a low-polarity and a polar solvent by viscosity measurements. In a low-polarity solvent (tetrahydrofuran (THF)), the ionomer that had a large number of ionic groups per chain (40–200) showed dominant intramolecular interaction at very dilute concentration and dominant intermolecular interaction at high concentration. However, the ionomer that had a small number of ionic groups per chain (1–3) showed almost no intramolecular interaction at dilute concentration and small degree of intermolecular interaction at high concentration. In a polar solvent (dimethylformamide (DMF)), even the ionomer with a very small number of ionic groups per chain (e.g., 1 on average) showed typical polyelectrolyte behavior. These experimental results suggest the important role of intermolecular interaction in the viscosity behavior of salt-free polyelectrolytes even in low-concentration solutions.

Introduction

Ionomers are a class of ion-containing polymers that have ions in concentrations up to 10–15 mol %, distributed in nonionic backbone chains. They have been mostly studied in the solid state.[1-4] This is in marked contrast to the situation with regard to polyelectrolytes, where major interest has been concentrated on solution properties.[5,6] Recently, however, the solution properties of ionomers have begun to be studied because of the realization of their unique properties.[7-21] In general, two types of behavior have been observed according to the polarity of solvent:[9] (1) aggregation behavior due to dipolar attractions in nonpolar solvents and (2) polyelectrolyte behavior due to Coulombic interactions in polar solvents.

In nonpolar solvents, ionomers tend to form aggregates due to the attraction between ion pairs in the medium of low dielectric constant: Lundberg and Phillips[9] showed that the reduced viscosity at low polymer concentration was lower than that of the ionomer precursor (polystyrene) due to the dominant intramolecular association of ion pairs, while the reduced viscosity at high polymer concentration was higher than that of polystyrene due to the dominant intermolecular association of ion pairs. Fitzgerald and Weiss[13] showed the existence of ionic aggregates for an ionomer with Cu^{2+} ion in solution by using ESR spectroscopy. It has been generally noticed that the aggregation is enhanced by increasing ion content.

In polar solvents, ionomers show polyelectrolyte behavior: Lundberg and Phillips[9] showed that the reduced viscosity of ionomers increased remarkably with decreasing polymer concentration. This polyelectrolyte behavior of ionomers can be suppressed by adding small salts such as LiCl.[7,19] MacKnight et al.[14] reported the broad single peaks in neutron scattering curves. Hara and Wu[18] showed that the reciprocal reduced scattered light intensity from ionomer solutions increased remarkably with increasing polymer concentration. All these phenomena have been observed for polyelectrolyte/water solutions.[5,6] However, it should be stressed that even the ionomer whose ion content is very small (for example, less than 1 mol %) shows polyelectrolyte behavior. Also, it has been generally noticed that the polyelectrolyte behavior of ionomers is enhanced by increasing ion content.

One of the essential factors that control the solution properties of polymers is the balance between the intramolecular interaction and the intermolecular interaction.[22] For example, viscosity measurements[9] for ionomers in a low-polarity solvent suggest that the intramolecular interaction dominates at dilute concentration, while the intermolecular interaction dominates at high concentration. Also, it is usually assumed that polyelectrolyte behavior in viscosity (in polyelectrolyte/water or ionomer/polar solvent) is due to the intramolecular repulsion between fixed ions in a polymer chain.[5,6,9] However, it was recently suggested that the intermolecular interaction may play an important role for the viscosity behavior of salt-free polyelectrolytes in water.[23,24] Although a variety of experimental data and theoretical considerations on the viscosity of salt-free polyelectrolytes in water have been obtained,[5,6,23] clear understanding has not been achieved. The viscosity behavior of salt-free polyelectrolytes is one of the unsolved problems.

Ionomers offer good model systems to investigate the characteristics of salt-free polyelectrolytes.[18] Since ionomers can be dissolved in polar organic solvents, we can avoid various problems associated with aqueous solutions, such as self-dissociation of solvent (water), complex water structure, etc. Also, ionomers in polar solvents have advantages in that relatively pure systems can be obtained, and solvents (therefore, the dielectric constant of the medium) can be varied and ion content can easily be varied. Moreover, measurements such as light scattering and viscosity are easier to conduct due to the strong scattering[18] and low viscosity[17] of ionomer solutions.

In this paper, we study the role of intra- and intermolecular interactions on the aggregation and polyelectrolyte behavior of ionomers by viscosity measurements. This was done by changing the number of ionic groups per chain, since it is expected that the importance of intramolecular interactions decreases with decreasing number of ionic groups per chain.

Experimental Section

Materials. Lightly sulfonated polystyrene was prepared by the sulfonation of polystyrene by using acetyl sulfate as a sulfonating agent.[25] The starting polystyrenes were polystyrene standards (Pressure Chemical Co.) with narrow molecular weight distributions ($M_w/M_n < 1.06$). Details about the preparation of lightly sulfonated polystyrene and their characterization were described elsewhere.[16,17] In this paper, the designation of ionomers is based on those proposed by Eisenberg;[2] S-xSSA-Na (M_w 400 000) means the copolymer of styrene (S) with sodium styrenesulfonate, whose mole fraction is x, and ionomer molecular weight is 400 000. Table I shows details about the samples employed. The molecular weight was obtained by light-scattering experiment on PS samples, ion content was obtained by the titration of acid groups, and the number of ionic groups per chain was calculated from these values.

Measurements. Polymer solutions were prepared by dissolving the freeze-dried ionomer samples in a proper solvent (DMF, THF)

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Table I
S-*x*SSA-Na Samples

mol wt	ion content, mol %	no. of ionic groups per chain
400 000	0	0
	0.94	36
	1.9	73
	3.2	122
	5.6	215
47 000	0	0
	0.24	1.1
	3.97	18
	5.82	26
9 000	0	0
	2.1	1.8
	4.0	3.5
	6.3	5.5
3 500	0	0
	2.0	0.67
	5.6	1.9
	8.1	2.7

under stirring for a day at room temperature. Polymers were easily dissolved except for the high molecular weight (400 000) ionomer samples with high ion content (5.6 mol %) in THF. The reduced viscosity was measured with a modified Ubbelohde viscometer at 25 ± 0.05 °C in a thermostated bath. The viscometer had a sintered-glass filter to remove dust particles and had caps to prevent evaporation of solvent and exposure to air. The measurement at each concentration was carried out until the relative error of three successive measurements became less than 0.5%. Extensive care was given to low molecular weight samples, where flow time was small, to obtain reproducible data; for these samples, the adjustment of the capillary position along the vertical direction and careful cleaning of all glassware, especially of the capillary, were essential to obtaining good data.

Results and Discussion

Aggregation Behavior. It has now been widely recognized that ionomers in low-polarity or nonpolar solvents tend to aggregate due to attraction between ionic dipoles (ion pairs). This has been pointed out by various experiments, including viscosity,[8,9,11,16,17] light scattering,[15,16,21] neutron scattering,[20] and spectroscopy[13] measurements. Most widely studied is the viscosity behavior of various ionomers. Figure 1 shows the viscosity behavior of the S-*x*SSA-Na (M_w 400 000) system in a low-polarity solvent (THF) for various ion contents. The data from high molecular weight samples (Figure 1) are consistent with those reported by Lundberg et al.[9] for high molecular weight samples. The reduced viscosities at dilute polymer concentration decrease with ion content, while they increase with ion content at high polymer concentration. Similar results have been obtained for other ionomer systems.[11,16] Basically, this has been interpreted in terms of the association of ion pairs in a low dielectric constant medium:[9] at low polymer concentration, the viscosity of the ionomer solution is lower than that of the PS solution due to the dominant intramolecular associations between ion pairs, while at high polymer concentration the viscosity is higher than that of the PS solution due to the dominant intermolecular associations between ion pairs. Figure 1 also shows that the curve is concave up, which reflects the increasing aggregation with polymer concentration. Eventually, gels are formed at higher concentration. Figure 2 shows the intrinsic viscosity, [η], of the high molecular weight sample as a function of ion content. It is seen that the intrinsic viscosity decreases with ion content, which is attributed to the shrinkage of polymer chains due to intramolecular dipolar attractions. It is also seen that the ionomer chains are expected to collapse at about 5 mol % ion content.

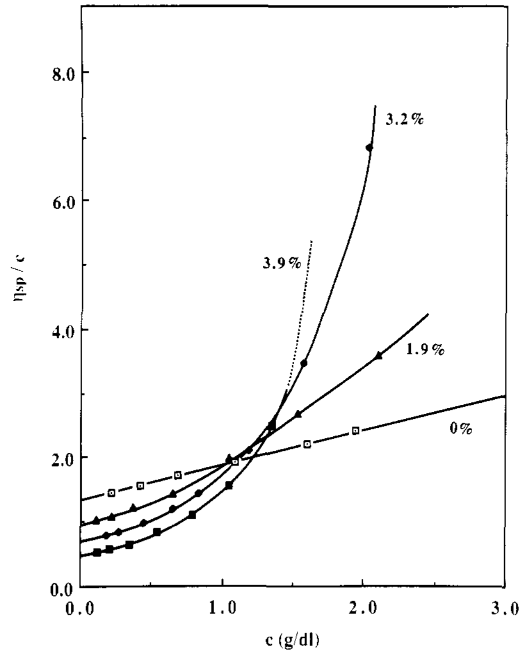

Figure 1. Reduced viscosity against polymer concentration for S-*x*SSA-Na (M_w 400 000) of various ion contents in THF.

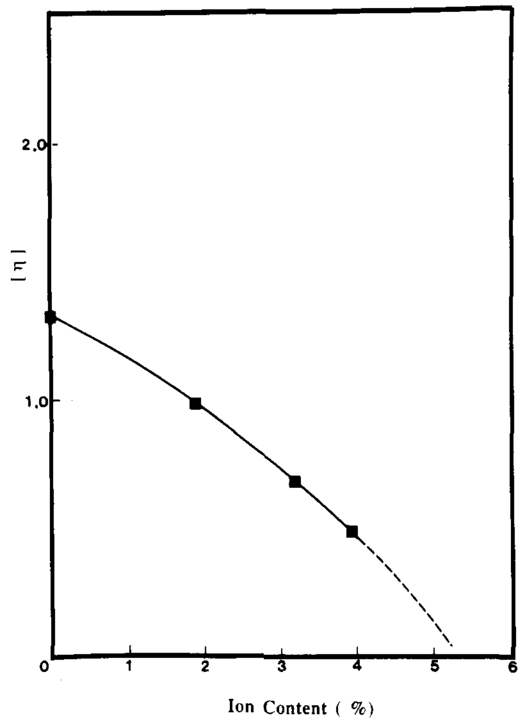

Figure 2. Intrinsic viscosity against ion contents for S-*x*SSA-Na (M_w 400 000) in THF.

However, the viscosity behavior of lower molecular weight samples (M_w 9000 and 3500) are different from that of high molecular weight sample as is shown in Figures 3 and 4: the reduced viscosity at low polymer concentration changes only slightly, and the overall curve is concave down. These phenomena can be explained by considering the number of ion pairs in a chain. Since the number of ion pairs per chain is very small for these samples (Table I), the intramolecular association causing the shrinkage of molecules is negligible. Therefore, intrinsic viscosities of these samples change only slightly as a function of ion content (Figures 5 and 6). Also, it is seen that the reduced viscosity at high polymer concentration for these samples increases gradually with increasing ion content (Figures

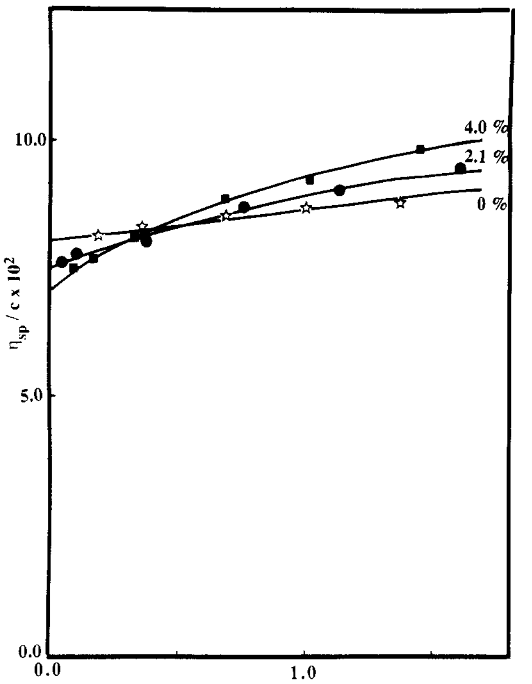

Figure 3. Reduced viscosity against polymer concentration for S-xSSA-Na (M_w 9000) of various ion contents in THF.

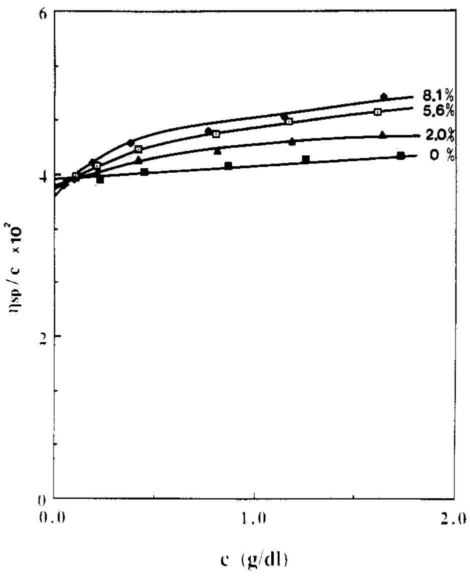

Figure 4. Reduced viscosity against polymer concentration for S-xSSA-Na (M_w 3500) of various ion contents in THF.

3 and 4), and the curves are concave down instead of concave up (as is the case of 400 000 samples). This is reasonable, since the intermolecular association is still effective for these ionomers, although the degree of aggregation is small. These results clearly indicate the role of intra- and intermolecular dipolar attractions of ionomers in a low-polarity solvent, which is consistent with Lundberg's ideas.[9]

Polyelectrolyte Behavior. It has been pointed out that ionomers show polyelectrolyte behavior in polar solvents. This has been shown by various methods, including viscosity,[7,9,11,16,17] light scattering,[15,18,21] and neutron scattering.[14] Most widely studied is, again, the viscosity behavior of various ionomers. Figure 7 shows the viscosity behavior of the S-xSSA-Na (M_w 400 000) system in a polar solvent (DMF) for various ion contents. This figure shows typical polyelectrolyte behavior: the reduced viscosity, η_{sp}/c, increases remarkably with decreasing polymer concentration. Also, it is seen that polyelectrolyte behavior is enhanced with increasing ion content. These data are consistent with those reported by Lundberg and Phillips[9] for high molecular weight samples.

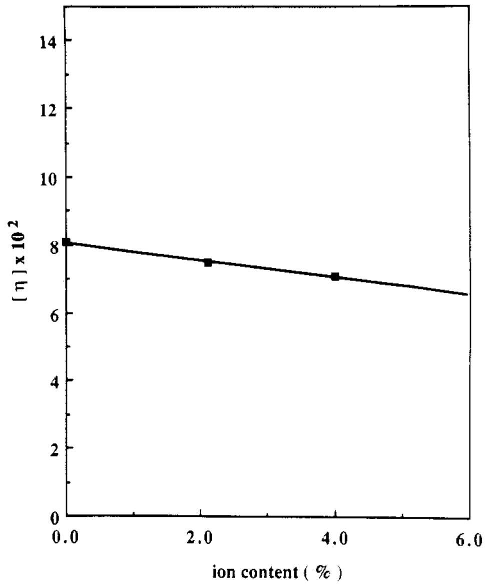

Figure 5. Intrinsic viscosity against ion contents for S-xSSA-Na (M_w 9000) in THF.

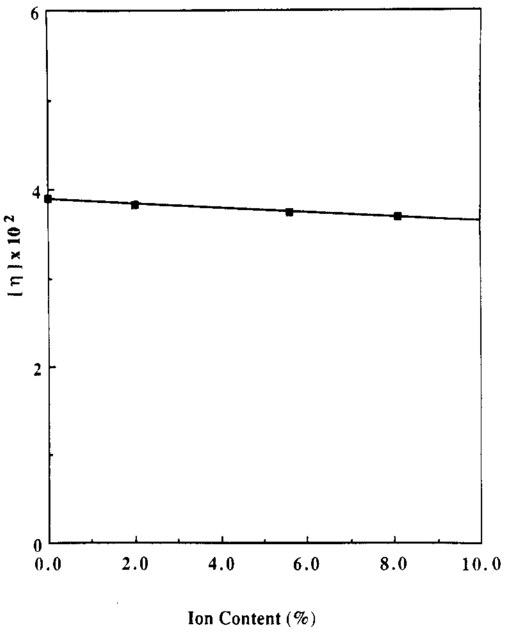

Figure 6. Intrinsic viscosity against ion contents for S-xSSA-Na (M_w 3500) in THF.

Figures 8 and 9 show the polyelectrolyte behavior of low molecular weight samples (M_w 9000 and 3500). Again, they all show the typical polyelectrolyte behavior, which increases with ion content. Although the number of ions per chain is very small for the low molecular weight samples (for example, the S-0.02SSA-Na (M_w 3500) sample has less than one ionic group per chain on average; Table I), they still show polyelectrolyte behavior.

To see whether molecular weight effects are involved, we also studied the polyelectrolyte behavior of ionomers with fairly high molecular weight (47 000) but with very low ion content (0.24 mol %; Figure 10); this sample has only 1.1 ions per chain on average. As is seen in Figure 10, the sample still shows polyelectrolyte behavior. Therefore, the polyelectrolyte behavior observed in low

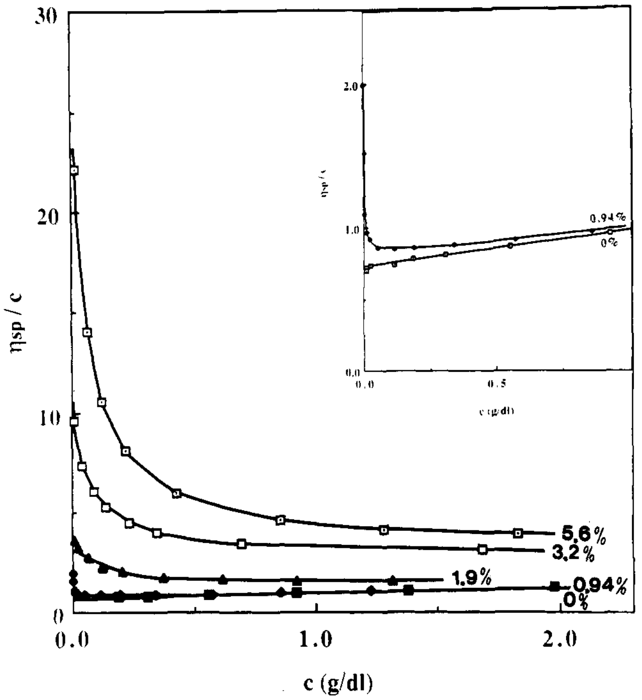

Figure 7. Reduced viscosity against polymer concentration for S-xSSA-Na (M_w 400 000) of various ion contents in DMF.

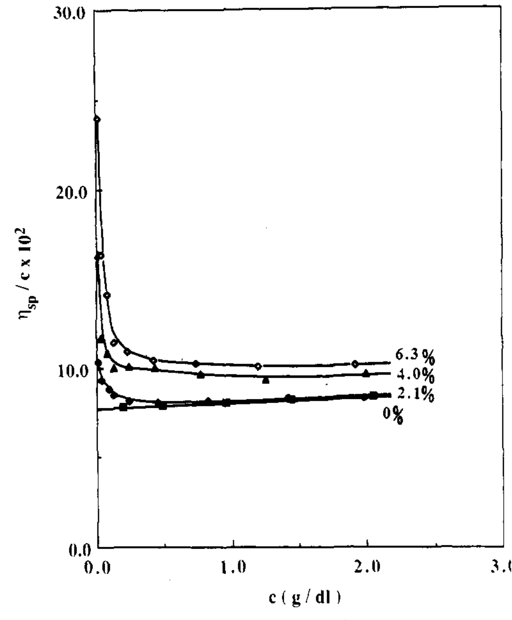

Figure 8. Reduced viscosity against polymer concentration for S-xSSA-Na (M_w 9000) in DMF.

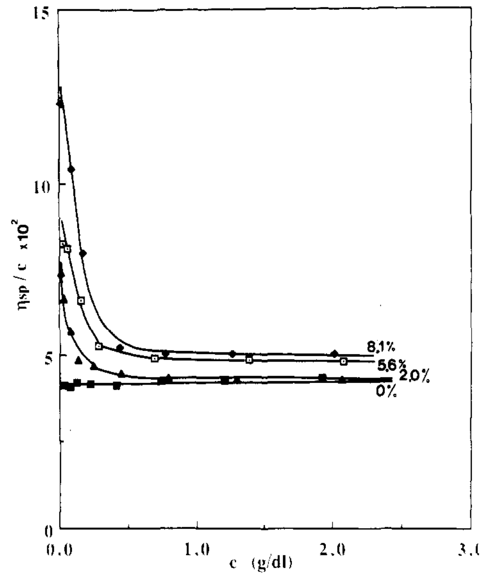

Figure 9. Reduced viscosity against polymer concentration for S-xSSA-Na (M_w 3500) in DMF.

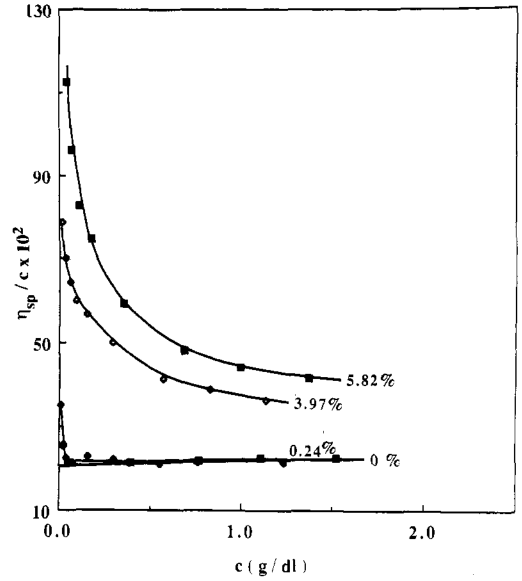

Figure 10. Reduced viscosity against polymer concentration for S-xSSA-Na (M_w 47 000) in DMF.

molecular weight samples appears to be similar to those observed in high molecular weight samples.

Since intramolecular repulsion is neglible for these systems, the conventional explanation of the viscosity behavior of polyelectrolytes, which is based on intramolecular repulsion between fixed ions on the same chain,[5,6] is difficult to apply to our data. While more detailed experiments are necessary to confirm this conclusion, this suggests the importance of intermolecular interactions rather than just the intramolecular interactions observed in the viscosity behavior of polyelectrolytes. These points were observed for polyelectrolytes in aqueous solution: Wolff[23] discussed that, in the concentration range where the Fuoss equation was applicable, chains were entangled and decreased in size with concentration. Also, Hara[24] et al.[26,27] suggested from the results of viscosity and light-scattering measurements that the intermolecular interaction was the major factor to determine the solution properties of polyelectrolytes in the concentration range where the Fuoss equation was applicable. An interesting finding relating to this behavior that should be mentioned here is the work by Lantman et al.[15] They studied dynamic light scattering of sulfonated ionomers in DMF and showed that the diffusion coefficient was constant in a concentration range where the reduced viscosity decreased remarkably with concentration. They suggested the importance of interference between ionomer chains even at low concentrations, which seems consistent with our results described above. Another interesting explanation has been proposed by Ise.[28] Instead of considering the repulsive interactions between polyelectrolyte molecules, they have considered the attraction between molecules, which comes from the net attraction of charges with the same sign, via counterions with opposite sign. This implies that the major factor determining the solution properties of polyelectrolytes is the intermolecular attractive interactions. Whether the interaction is attractive or repulsive, our data as well as the results described above suggest the importance of intermolecular interactions in the viscosity behavior of salt-free polyelectrolytes.

The premise of our discussion is that the polyelectrolyte behavior of ionomer/polar solvent systems is essentially the same as that for polyelectrolyte/water systems. The difference is in the degree but not the nature of the interaction. This comes directly from the experimental results: the viscosities of ionomer/polar solvent systems change exactly in the same way as the polyelectrolyte/water system as shown above. Also, it has been shown[19] that when small salts are added, polyelectrolyte behavior is suppressed in the same manner as in polyelectrolyte/water systems. The "abnormal" light-scattering behavior of an ionomer/polar solvent system[18,21] is exactly the same as that observed in a polyelectrolyte/water system,[29,30] except that the absolute value of reciprocal reduced scattered intensity from the ionomer system is smaller. Also, the broad single peak observed in small-angle neutron scattering experiments was also reported for an ionomer/polar solvent system,[14] which is usually observed in polyelectrolyte/water systems. Moreover, the characteristic behavior of polyelectrolyte/water systems, such as counterion binding, was observed.[7,17] If this is the case, high charge density is not a necessary condition to cause polyelectrolyte behavior. The only necessity appears to be the existence of ionic group(s) in polymer chains, whatever their number is.

Conclusions

The effect of intra- and intermolecular interactions on sulfonated polystyrene ionomers was studied in a low-polarity and a polar solvent by viscosity measurements. In a low-polarity solvent (THF), the decrease in intrinsic viscosity, which was attributed to the shrinkage of polymer chains, was observed for ionomers having a large number of ion pairs per chain (40–200). However, the decrease in intrinsic viscosity was negligible for the ionomers that had a very small number of ion pairs per chain (1–3). This was explained in terms of the absence of intramolecular dipolar attraction in these samples.

Polyelectrolyte behavior was observed in a polar solvent (DMF) for ionomer samples that had a very small number of ionic groups per chain (1–3) as well as for samples with a large number of ionic groups per chain (40–200). It is suggested that the intermolecular interaction played an major role in the viscosity behavior of salt-free polyelectrolytes even in dilute solution. This is an important subject for further study. Light-scattering experiments are currently being conducted to elucidate the structure and will be reported.

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